

Synthesis, Characterization and Application of Hydrophilic Copolymers on Physico-mechanical Properties of Cement Pastes

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Abstract: A series of poly[2-hydroxy ethyl acrylate (2-HEA)-co-styrene (St)] was prepared by solution polymerization technique in alcoholic solution using azo-bis-isobutyro-nitril (ABIN) as initiator. The hydrophilic copolymers were characterized by FT-IR, ¹H NMR, mass spectra, viscosity, DSC and TGA. The effect of addition of hydrophilic copolymers with and without sodium hydroxide on the physico-mechanical properties of ordinary Portland cement (OPC) pastes was studied. The results showed that the addition of hydrophilic copolymers with and without sodium hydroxide to the cement increase the setting time, combined water content and compressive strength. The results of the solution of the prepared copolymers in presence of sodium hydroxide are better than its polymers without sodium hydroxide.

Key words: Solution polymerization • Portland cement • Setting • Combined water • Compressive strength

INTRODUCTION

Polymer-modified cement is today a valuable help in the production of high performance concrete, which exhibits high flow, workability, high density and durability on setting. In spite of the practically valuable properties of polymer-modified cement, the microstructure of this material is not clear because its observation by microscopy is difficult [1-3]. However, worldwide usage of polymers, understanding the mechanisms through which they act is still an object of much study [4-8].

Ordinary Portland cement (OPC) is a finely ground mixture of a clinker (composed of lime, silica, alumina, iron oxide and small amounts of alkalis) and a set retarder (usually hydrated calcium sulfate or gypsum). A sample mineralogical composition of Portland cement clinker [9] is given in Table 1. The optimum gypsum content in cements is usually in the range of 3-5% SO₃ (S) [10].

Cement particles in suspension or paste are encountered in the form of agglomerations of primary particles interconnected by forces ranging from very weak ones to chemical bonds. Introduction of the admixture separates cement agglomeration into smaller fragments or primary particles [11].

The consequences of the polymer/cement interaction depend on the physicochemical parameters of the cement and the polymers [7, 12]: chemical nature of the polymers; average molecular weight and its distribution; actual dosage and admixture introduction method; cement type, including fineness, phase composition and alkali/sulfate content; form of calcium sulfate (gypsum, hemihydrate, anhydrite, synthetic calcium sulfate).

The effect of such polymers on the rheology of cement pastes was studied by Negim *et al.* [13-22]. The results show that the addition of polymers to the cement improves most of the specific characteristics of OPC.

Table 1: The chemical composition of the raw materials, mass %

Oxides Materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	L.O.I
PCC	21.48	6.03	4.22	64.29	0.68	0.39	0.21	0.11	1.32
Gypsum	0.58	0.14	0.11	30.08	0.13	45.36	0.07	0.09	22.16

The present work aimed to study the preparation and characterization of poly [2-hydroxy ethyl acrylate (2-HEA)-co-styrene (St)] via FT-IR, ¹H NMR, mass spectra, viscosity, DSC and TGA. The work was further extended to investigate the application of the obtained copolymer to modify the workability of cement pastes.

MATERIALS AND METHODS

Synthesis and Characterization of Copolymers:

Hydrophilic copolymers based on 2-hydroxy ethyl acrylate (2-HEA) and styrene (St) was synthesized with composition ratios (M1 = 95: 05, M2 = 90: 10, M3 = 85: 15) using ABIN as an initiator and ethanol as a solvent at 60 °C. The copolymers synthesized were reprecipitated several times from ethanol to diethyl ether and dried in vacuum desiccators at 30°C until a constant weight was achieved. The copolymer was prepared in the presence or absence of sodium hydroxide solution. The prepared polymers were characterized by FT-IR, ¹H NMR spectra, viscosity, mass spectra, DSC, TGA. The FT-IR analysis of the prepared polymers was carried out using Perkin Elmer FT-IR. The ¹H NMR spectra of the prepared polymers were carried out using A JEOL EX-270 NMR spectrometer, 270 MHz for ¹H NMR was used with super conducting magnet Oxford and 5 mm Dual probe head for ¹H and ¹³C - analysis. Typical conditions are spectral width 4000 Hz for ¹H and 15000 Hz for ¹³C; 32 K data points and flip angle of 45°. Thermogravimetric analysis (TGA) was recorded on a TGA/SDTA851e, METTLER TOLEDO. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N₂ flow at 20 mL min⁻¹. The measurements were carried out between -50°C and 200°C at a heating rate of 10°C Min⁻¹. The viscosity of polymer solution was measured at 25 ± 0.1 °C using an Ubbelohde viscometer.

Raw materials: The raw materials used in the present study are Portland cement clinker (PCC) and raw gypsum (G), which were provided by The National Cement Company, El-Tebbin, Egypt. Each of those raw materials was separately ground in a steel ball mill until the surface area of 3650 and 2800 cm²/g, respectively were achieved. The chemical composition of the raw materials is shown in Table 1. The mineralogical composition of the PCC

sample is C₃S, 58.79 %; C₂S, 17.68 %; C₃A, 8.08 %; C₄AF, 9.72 %. The Ordinary Portland Cement (M₀) was prepared by mixing 96 wt. % PCC and 4 wt. % G in a porcelain ball mill for one hour using 3 balls to assure complete homogeneity of the cement. The Blaine surface area[23] of the cement sample was 3350 cm²/g.

Preparation and methods: The prepared copolymer (either in the absence or presence of NaOH) was added to mixing water and then added gradually to 300 g of the dry cement in order to determine the water of consistency and setting time using Vicat apparatus[24, 25]. Workability test using the flow table was conducted as per BS 1881: part 105, 1984. The determined water of consistency premixed with the copolymer was added to 500 g of the dry cement. The resulting cement pastes were directly moulded into one-inch cube stainless steel moulds. The moulds were manually agitated for 2 minutes and then on a vibrator for another 2 minutes to assure the complete removal of air bubbles and voids and to produce suitable pastes. The moulds were kept in a humidity chamber at 100 % R. H and a constant room temperature over night, then demoulded and cured under water till the time of testing (1, 3, 7 and 28 days) for total porosity and compressive strength [26]. The compressive strength was carried out using a hydraulic testing machine of Type LPM 600 M1 SEIDNER (Germany) having full capacity of 600 KN. The loading was applied perpendicular to the direction of the upper surface of the cubes. The total porosity, ξ of each sample at any interval was calculated from the following equation [26]:

$$\xi = 0.99 \times W_e \times dp / (1 + W_t)$$

where 0.99 is the specific volume of the free water, W_e is the evaporable water content, dp is the bulk density, g/cm³ and W_t is the total water content which is equal to the sum of evaporable water (W_e) and combined water (W_n) contents. The bulk density (dp) was determined from the following equation: $dp = W_1 / (W_1 - W_2)$ g/cm³, where W_1 is the saturated surface dry weight in air (g) and W_2 is the submerged weight in water (g). To stop the hydration at any age of hydration, a representative sample of about 10 g after the determination of compressive strength was taken, ground in an alumina mortar containing 50 ml of 1:1 (methanol: acetone) solution mixture and then filtered through a sintered glass funnel

(G4). The sample was washed with 50 ml fresh diethyl ether, dried at 70 °C for one hour and then kept inside an airtight bottle as described elsewhere [27]. The curing water was renewed every week. The combined water content (Wn) of samples predried at 105°C for 24 hours was determined as the ignition loss at 1000°C for 30 minutes [28].

RESULTS AND DISCUSSION

FT-IR Spectra of the Prepared Polymers: FT-IR spectra of the prepared copolymers with St are shown in Figure 1a, b. It is shown from the Figure that, there are small differences in the characteristic peaks of the copolymers due to copolymerization.

Fig. 1(a) showed that the main characteristic peaks of 2-HEA are at 3398 cm^{-1} (O-H stretch), 2950 cm^{-1} (C-H stretch) and 1637 cm^{-1} (C=O). For the spectrum of copolymer, in Fig. 1 (b), some new absorption peak appeared. The peak at 1636 cm^{-1} corresponds to the C=C vibrations of St introduced onto the 2-HEA. Some peaks are shifted to higher intensity due to copolymerization such as, 1725 cm^{-1} (C=O) and 3398 cm^{-1} (O-H stretch).

^1H NMR spectra of prepared polymers: The ^1H NMR spectra of the prepared homo (HEA) and its copolymer with St are shown in Figure 2 and Table 2.

Mass Spectra of the Prepared Polymers: The characteristic peaks of the mass spectra of the prepared copolymer of (2-HEA-co-St) are shown in Table 3 and Figure 3. It is clear from the Table 3, that there are characteristics peaks numbers such as 66 and 164, which confirm the structures of the prepared polymers.

Viscosity and T_g of the Prepared Copolymers: Viscosity of the prepared homo 2-hydroxyethyl acrylate and its copolymer with St is shown in Table 4. It is clear that, the viscosity of the copolymer increased with increasing the ratio of styrene from 5 to 15 wt.%.

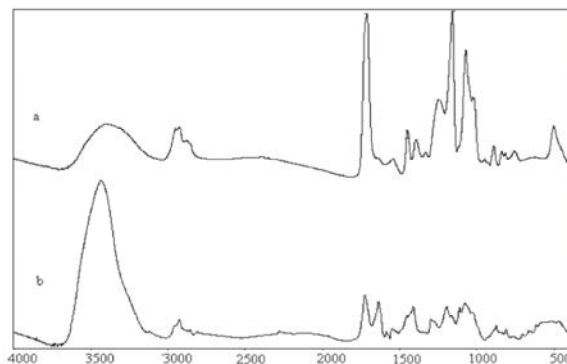


Fig. 1: FT-IR spectra of prepared polymers:
(a): poly[2-HEA] and (b): poly[2-HEA-co-St].

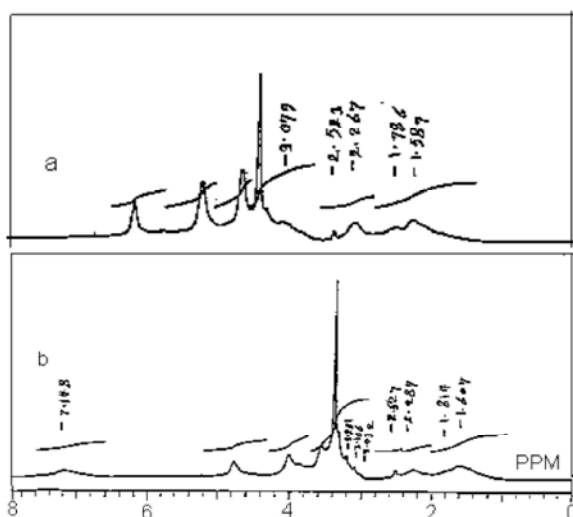


Fig. 2: ^1H NMR spectra of prepared polymers:
(a) poly[HEA] and (b) poly[HEA-co-St].

The results of DSC analysis of copolymer are summarized in Table 4. It was found that experimentally measured T_g values closely follow the predictions of the fox equations. However, the T_g of the copolymer increased with increasing the ratio of styrene in the copolymer. The increase of T_g of the copolymer is mainly due to the increase of hard segment in the structure of copolymer.

Table 2: Chemical shifts of prepared polymer

Polymers	Resonance Signal (PPM)	Proton	Assignment
[2-HEA]	1.58 - 1.78	-CH ₂ - (a)	$\left(\text{CH}_2^{\text{a}} - \text{CH}^{\text{b}} \right)_n$ $\text{COOCH}_2^{\text{c}}\text{CH}_2^{\text{d}}\text{OH}$
	2.26 - 2.25	-CH- (b)	
	4.00 - 4.02	-CH ₂ - (c)	
	3.38 - 3.56	-CH ₂ - (d)	
[2-HEA-co-St]	1.60 - 1.81	-CH ₂ - (a)	$\left(\text{CH}_2^{\text{a}} - \text{CH}^{\text{b}} \right)_n \left(\text{CH}_2^{\text{a}} - \text{CH}^{\text{b}} \right)_m$ $\text{COOCH}_2^{\text{c}}\text{CH}_2^{\text{d}}\text{OH}$ $\text{C}_6\text{H}_5^{\text{e}}$
	2.28 - 2.52	-CH- (b)	
	4.01 - 4.02	-CH ₂ - (c)	
	3.34 - 3.38	-CH ₂ - (d)	
	7.148	-CH- (e)	

Table 3: Mass spectra of the prepared of poly [2-HEA-co-St].

No. of peak	Mass	Fragment
5	54	$\left(\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \right)^{\cdot}$
28	77	$\left(\text{C}_6\text{H}_5 \right)^{\cdot}$
40	89	$\left(\text{CH}_2 - \text{CH}_2 - \text{O} - \overset{\text{O}}{\parallel}{\text{C}} \right)^{\cdot}$ OH
54	104	$\left(\text{CH}_2 - \text{CH} \right)^{\cdot}$ C_6H_5
66	116	$\left(\text{CH}_2 - \text{CH} \right)^{\cdot}$ $\text{COOCH}_2\text{CH}_2\text{OH}$
164	220	$\left(\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \right)^{\cdot}$ $\text{COOCH}_2\text{CH}_2\text{OH}$ C_6H_5

Table 4: Viscosity of the prepared copolymers.

Copolymer	Feed	T_g^a	T_g^b	η
[2-HEA-co-St]	M1	-10.96	-12.33	0.175
	M2	-6.79	-7.98	0.343
	M3	-2.49	-3.69	0.455

^apredicted using Fox equation

^b measured using DSC

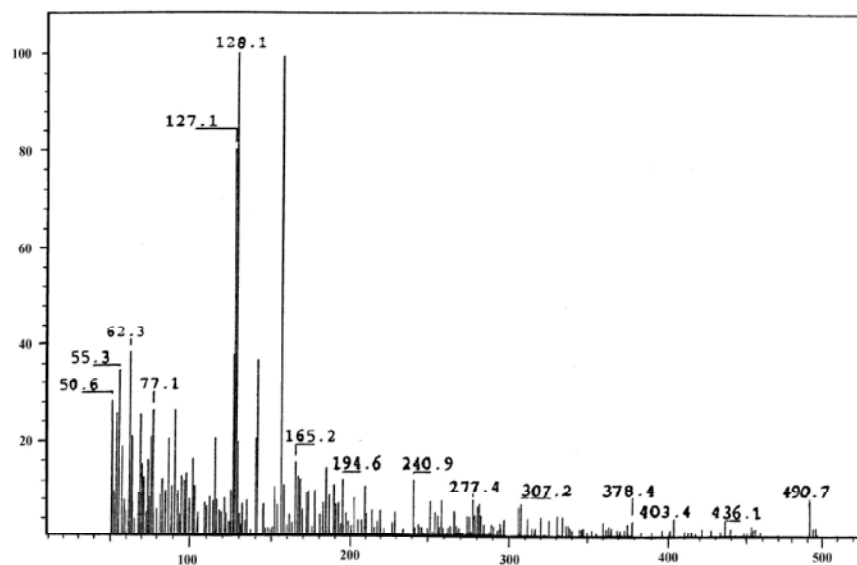


Fig. 3: Mass spectra of prepared poly[2-HEA-co-St].

Table 5: Thermal properties of poly [2-HEA-co-St]

Copolymer	Temperature range, °C	Weight lost, wt. %	Residue, wt. %	IDT, °C	PDT _{max} , °C
M1	30.11 - 159.13	9.36	91.1	295	420
	159.13 - 356.91	40.23	50.8		
	356.91 - 887.94	29.57	21.29		
M2	29.85 - 151.90	9.40	90.56	300	420
	151.90 - 362.29	45.82	44.74		
	362.29 - 898.07	28.68	16.06		
M3	29.60 - 152.75	9.70	90.73	320	00
	152.75 - 252.35	5.10	85.60		
	252.35 - 894.66	64.25	21.34		

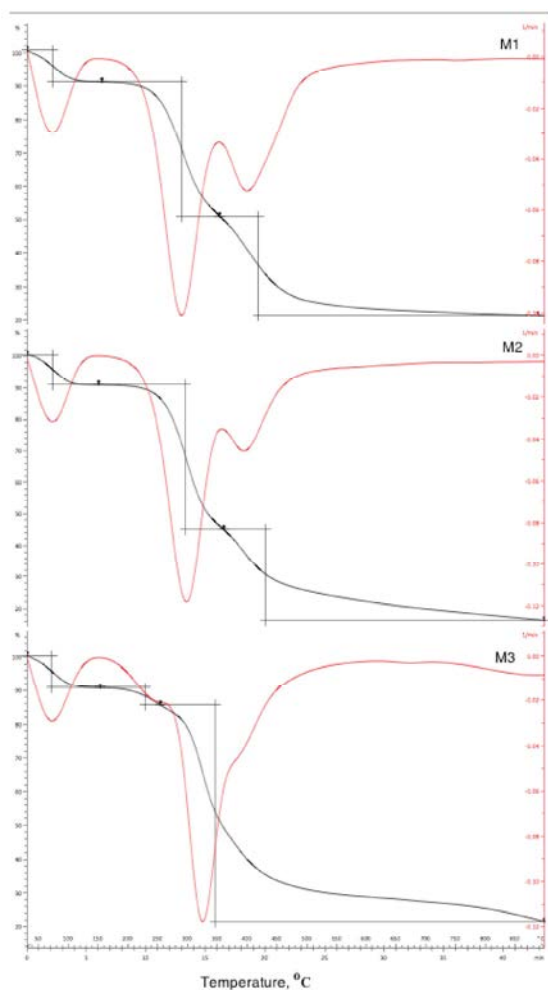


Fig. 4: TGA curves for P[2-HEA-co-St].

Thermogravimetric Analysis (TGA): Figure 4 and Table 5 summarize the TGA results of P[2-HEA-co-St] with composition ratio was M1, M2 and M3. These TGA's were performed from 20°C to 898°C at 20°C/min in air. It is clear that the thermal degradation process for P[2-HEA-co-St] sample proceeds in three steps as shown in Figure 4 and Table 5. The first weight loss occurs between

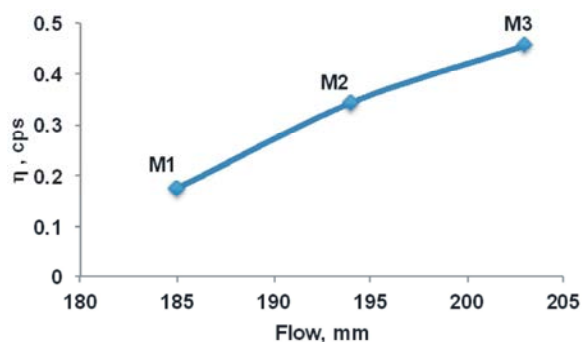


Fig. 5: The effect of viscosity of copolymer on the flow of OPC pastes.

29 and 159°C, which corresponds to the removal of solvent and water. In the second and third steps, in the range of 159-894°C and weight loss (85-21%) are attributed to the decomposition of P[2-HEA-co-St].

The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared at 420 °C for M1 and M2. On the other hand, initial degradation temperature (IDT) increased with increasing the ratio of styrene in the copolymer. For temperatures higher than 300°C, M3 films show a higher weight loss than M1 and M2 films.

Application of Hydrophilic Copolymers for Cement

Flow: The effect of copolymers on flow of fresh OPC with W/C ratio 0.28 is shown in Figure 5. It is seen that the addition of copolymers to OPC pastes increased the flow from 165 mm to OPC (M0) to 185 mm, M1, 194 mm to M2 and 203 mm to M3. The flow of cement effect generally proportional to the amount of the added latex and depends on the monomer composition, and/or protective colloids present in the latex and viscosity of the latex [29, 30]. Figure 5 shows that the flow of OPC pastes increases with increasing viscosity of the copolymers.

Water/Cement Ratio: The importance of the water/cement ratio was rapidly recognized as the most important factor governing strength properties [4]. The optimum W/C ratio of the pure OPC (M0) was 0.28, which decreases to 0.25 and then become constant even with increasing the hydrophilic polymer concentrations. In a general sense, polymer modified cement are often used as high-range water reducers, to make concrete stronger by lowering the water/cement ratio [4]. To achieve water reduction level as high as 25 percent, polymers have to be used at high dosages ranging between 0.25 and 1.0 g/L. As the water-cementitious materials ratio was decreased, unexpected behavior was sometimes experienced with particular cement-superplasticizer combinations, despite the fact that both components satisfied their respective acceptance requirements. With time, these types of phenomena become more frequent, especially in case of very low water-cementitious materials ratio concrete. Such phenomena are usually referred to as cement-polymer incompatibility [4].

Setting Time: The variation of setting time of pastes prepared by adding solutions of copolymers with and without sodium hydroxide are shown in Figures 6 and 7. It is clear that the setting time (initial and final) increase sharply with the increase of the polymer concentrations. This is due to the negative electrical charge so produced prevents adhesion and flocculation of particles and prolongs setting time [31-34]. In addition, the setting time increases gradually as the ratio of styrene in the hydrophilic copolymer increases. Although the initial and final set are delayed by adding the polymer, the delay and the time between initial and final set are more increased by adding solution of copolymers without sodium hydroxide than by adding the solutions of copolymer in presence of sodium hydroxide. Normal set is caused by C - S - H produced by the vivid hydration of alite. Since the solutions of hydrophilic polymers in absence of sodium hydroxide produces the complex salt with Ca^{2+} in the liquid phase more than the solutions of copolymer in presence of sodium hydroxide and reduces the concentration of Ca^{2+} , the hydration of alite is delayed [35] resulting in delay of setting as illustrated in Figure 6. Since free CaO acts as a supplier of Ca^{2+} in the liquid phase at the initial stage, free CaO is useful for reducing the setting time.

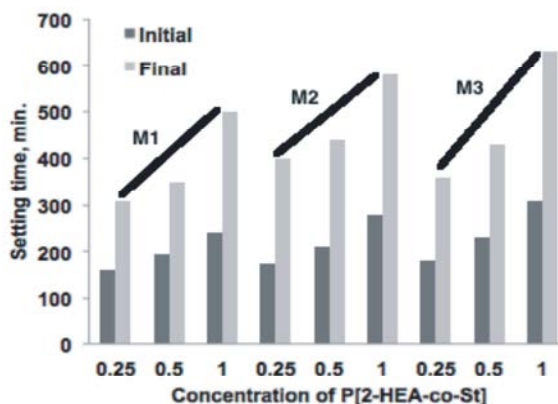


Fig. 6: The effect of concentration of copolymers on setting time of OPC pastes.

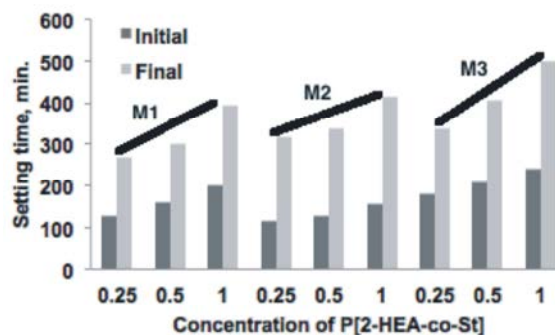


Fig. 7: The effect of concentration of copolymers in presence of NaOH on the setting time of OPC pastes.

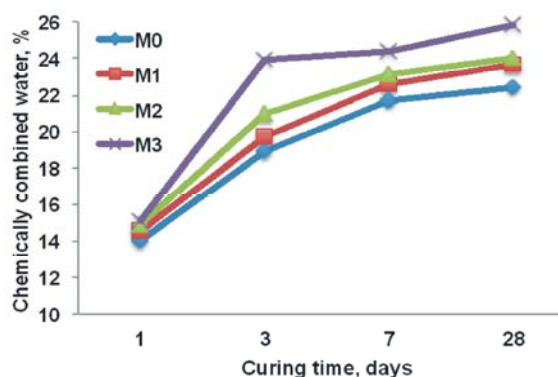


Fig. 8: The effect of P[2-HEA-co-St] on the chemically combined water content of OPC pastes.

Chemically Combined Water Content: The chemically combined water content of the various pastes premixed by adding the admixture (hydrophilic copolymers) with and without sodium hydroxide to OPCs is shown in Figures 8 and 9. The combined water generally increases as the curing time proceeds up to 28 days of hydration. This is because admixtures having a function group producing a

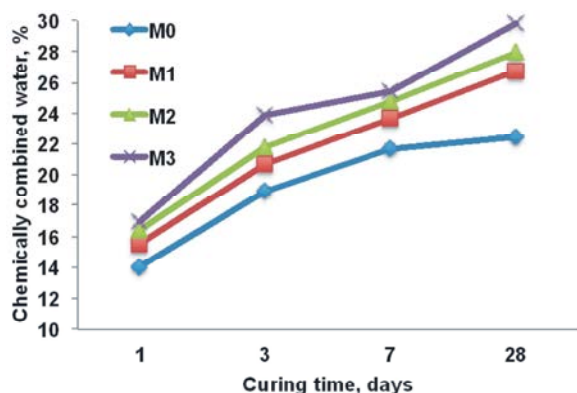


Fig. 9: The effect of P[2-HEA-co-St] in presence of NaOH on the chemically combined water content of OPC pastes.

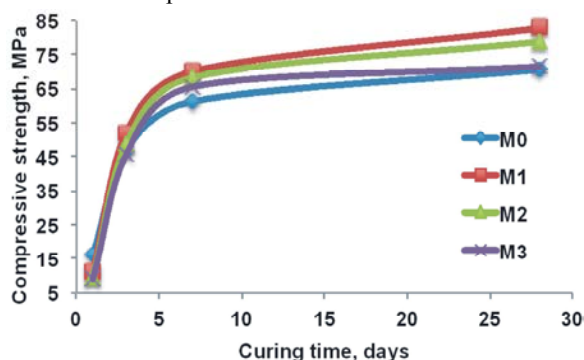


Fig. 10: The effect of P[2-HEA-co-St] on the strength of OPC pastes.

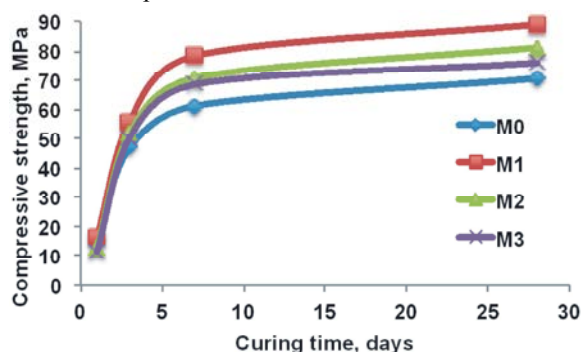


Fig. 11: The effect of P[2-HEA-co-St] on the compressive strength of OPC pastes in presence of NaOH.

complex salt with Ca^{2+} in the liquid phase at the early stage of hydration and accelerates the production of large ettringite crystals [36]. However, the combined water content increased as the ratio of styrene decreased in copolymers. Also, the combined water of pastes prepared by adding solutions of copolymers in presence of sodium hydroxide is larger than that in paste prepared by adding solutions of copolymers in absence

of sodium hydroxide. This is essentially attributed to the fact that the adsorption of admixtures to the particles of cement or cement hydrate depends upon the kinds of admixture and it depends upon the kinds of clinker minerals and hydrates when the kinds of admixture are the same [36].

Compressive Strength: The results of compressive strength of various cement pastes mixed with hydrophilic polymers, which are prepared by different concentrations, are represented as a function of curing time in Figures 10 and 11. As shown from Figure 10, the compressive strength values of the pastes premixed with the solutions of copolymers are lower during the early ages of hydration up to 3 days and then become higher during the latter ages up to 28 days. This is mainly due to the continual formation of hydration products, which tend to deposit into the pore structure of hardened cement cubes. This leads to a noticeable decrease in the total porosity. Therefore, the bulk density improves and the compressive strength is accordingly enhanced [37]. However, the compressive strength of pastes increases as the ratio of styrene decreased.

The compressive strength values of the pastes premixed with the solutions of copolymers in presence of sodium hydroxide increase sharply with curing time up to 28 days, as shown in Figure 11. This is principally due to the gradual increase in the process of polymerization or crystallization resulting from an increase in the branching of the used water-soluble copolymeric materials [38]. From Figures 10 and 11, the compressive strength of the pastes increases as the ratio of styrene in the copolymer decreases. In addition, the compressive strength of pastes which are prepared by adding solutions of copolymer in presence of sodium hydroxide are larger than that are prepared by adding solution of copolymer without sodium hydroxide. The addition of sodium hydroxide or the presence of residual alkalis in the superplasticizer enhances the early age strength of the mortars and concretes [39]. Moreover, the compressive strength of all samples is higher than that of the pure Portland cement nearly at all curing periods. This is mainly because the adhesive action, due to polymerization or crystallization of the polymeric materials, could cements the grains of the cement with each other associating them. Moreover, the excess of the polymer deposits and polymerizes within the pore system of the hardened cement cubes. The growth of crystalline structure act as nuclei for other ingredients. This may be continued to enlarge crystals and strong arms-bearing high strength [40].

CONCLUSIONS

Hydrophilic copolymers of 2-HEA with St in three different ratio ca. [(95: 05) M1, (90: 10) M2 and (85: 15) M3] were prepared and characterized in relation to FT-IR, ¹H NMR, DSC, TGA, mass spectra and viscosity.

Mixing of Portland cement powder with water that is premixed with the hydrophilic copolymers with and without sodium hydroxide evidently improves most of the specific characteristics of the cement pasts.

The W/C-ratio decreases, i.e. the hydrophilic copolymers with and without sodium hydroxide act as a water reducing agent when mixed with the cement powder.

The chemically combined water content and compressive strength of the solutions of hydrophilic copolymer in presence of sodium hydroxide also enhances and seems to be higher than that of its copolymers without sodium hydroxide and the pure Portland cement pastes nearly at all curing ages. As the ratios of St in the copolymer decrease, the properties of the cement pastes are also improved.

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